

PTO 07-5164

CC = JP  
20001107  
Kokai  
12311928

METHOD FOR DETERMINING THE NITROGEN CONCENTRATION IN A GATE OXIDE FILM  
[Geto sankamaku chu no chisso nodo hantei hoho]

Hiroshi Iwata

UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, D.C. JUNE 2007  
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY (19): JP

DOCUMENT NUMBER (11): 12311928

DOCUMENT KIND (12): Kokai

PUBLICATION DATE (43): 2000-0711

APPLICATION NUMBER (21): 11121090

APPLICATION DATE (22): 19990428

INTERNATIONAL CLASSIFICATION<sup>7</sup> (51): H 01 L 21/66  
29/78

INVENTOR (72): Hiroshi Iwata

APPLICANT (71): 000005049  
Sharp Corp.

TITLE (54): METHOD FOR DETERMINING THE  
NITROGEN CONCENTRATION IN A GATE  
OXIDE FILM

FOREIGN TITLE [54A]: Geto sankamaku chu no chisso nodo hantei  
hoho

## Claims

1. A method for determining the nitrogen concentration in a gate oxide film characterized by the fact that in the process of manufacturing semiconductor devices in which re-oxidation treatment is performed using a heating oven in an oxidative atmosphere after formation of a nitride oxide film by treating the thermal oxide film formed on a semiconductor substrate in a nitriding atmosphere using a heating oven, the nitrogen concentration in the thermal oxide film is determined from the deposition rate of the thermal oxide film in said re-oxidizing treatment.
2. The method for determining the nitrogen concentration in a gate oxide film described in Claim 1 characterized by the fact that the deposition rate in the re-oxidizing treatment is determined from the difference between the film thickness after formation of the nitride oxide film and the film thickness after re-oxidizing treatment.
3. The method for determining the nitrogen concentration in a gate oxide film described in Claim 1 or 2 characterized by the fact that in the re-oxidizing treatment, a hydrochloric acid oxidizing method is adopted.

## Detailed explanation of the invention

### Technical field of the invention

The present invention pertains to a method for determining the nitrogen concentration in a gate oxide film formed in the process of manufacturing a semiconductor device.

### Prior art

In the prior art, in order to minimize the problem of flat band voltage shift and interface level density increase due to hot carrier injection when the gate oxide film is formed Japanese Kokai Patent

Application No. Hei 1[1989]-37027 discloses a method in which re-oxidizing treatment is performed in an oxidative atmosphere using a short-term heating oven after a thermal oxide film formed on a silicon substrate has been treated in a nitriding atmosphere in a short-term heating oven to form a nitride oxide film. In said thermal oxidizing nitriding treatment, the nitrogen concentration in the gate oxide film varies as a function of the parameters, such as treatment time the nitrogen-containing gas gas flow rate, treatment temperature, etc., and the electrical characteristics vary correspondingly. Consequently, in order to obtain the desired electrical characteristics, the electrical characteristics of samples of the gate oxide film formed in tests are quantitatively analyzed by means of secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES), and other analysis devices, and the parameter values are set based on the results of said quantitative analysis.

#### Problems to be solved by the invention

However, in order to obtain a gate oxide film with the desired electrical characteristics, said analysis should be done each time the operation is performed, and this requires many man-hours and much cost. Also, in a semiconductor manufacturing plant, since the gate oxide film deposition treatment conditions are checked using the aforementioned method for every 200 device wafers treated on a regular basis to determine if the gate oxide film quality has the target electrical characteristics, it is impossible to check all the wafers for the desired electrical characteristics of the gate oxide films deposited on them. The purpose of the present invention is to solve the aforementioned problems of the prior art by providing a scheme characterized by the following facts: by exploiting the phenomenon that when nitrogen atoms are mixed in the atom bonds near the silicon substrate/oxide film interface, the nitrogen concentration in the gate oxide film becomes higher and the oxidation growth rate falls, the nitrogen concentration in the gate oxide film can be determined from the re-oxidized film thickness [change] rate, which is computed

easily by means of film thickness measurement without using SIMS, AES, or other measurement equipment.

#### Means to solve the problems

As Claim 1, the present invention provides a method for determining the nitrogen concentration in a gate oxide film characterized by the fact that in the process of manufacturing semiconductor devices in which re-oxidation treatment is performed using a heating oven in an oxidative atmosphere after formation of a nitride oxide film by treating the thermal oxide film formed on a semiconductor substrate in a nitriding atmosphere using a heating oven, the nitrogen concentration in the thermal oxide film is determined from the deposition rate of the thermal oxide film in said re-oxidizing treatment. As Claim 2, the present invention pertains to the method for determining the nitrogen concentration in a gate oxide film described in Claim 1 characterized by the fact that the deposition rate in the re-oxidizing treatment is determined from the difference between the film thickness after formation of the nitride oxide film and the film thickness after re-oxidizing treatment. Also, as Claim 3, the present invention pertains to the method for determining the nitrogen concentration in a gate oxide film described in Claim 1 or 2 characterized by the fact that in the re-oxidizing treatment, a hydrochloric acid oxidizing method is adopted.

#### Embodiment of the invention

In the following, an embodiment of the invention will be explained. Figure 1 shows an example of oxide film formation in this invention. Thermal oxide film (2) is formed on semiconductor substrate (1) using a CVD method (Figure 1a). Then, a nitride oxide film (3) is formed by means of short-term heating in a nitrous oxide atmosphere (Figure 1b). Then, the nitride oxide film is re-oxidized by means

of short-term heating (T) in an oxygen atmosphere to form re-oxidized film (4) (Figure 1c). The re-oxidized film thickness rate is computed using the formula  $[(L_2 - L_1)/T]$ , where  $L_1$  represents the film thickness after formation of the nitride oxide film by means of  $N_2O$  oxidation (nitriding oxidizing), and  $L_2$  represents the film thickness after subsequent re-oxidizing treatment. Here, said film thickness is determined using an optical film thickness measurement unit, and the target film thickness of the thermal oxide film is 40 Å. Figure 2 is a diagram illustrating the relationship between the nitrogen/oxygen peak intensity ratio determined by SIMS measurement when the parameter values of treatment time, treatment temperature, gas flow rate, etc., in the thermal oxidizing nitriding treatment are changed and the re-oxidized film thickness rate. For example, in plot A shown in Figure 2, the peak intensity ratio of nitrogen/oxygen determined by SIMS measurement is 0.0191, the  $N_2O$  flow rate is 5 slm, the treatment temperature is 900°C, the treatment time is 5 min, and the re-oxidizing rate is 0.88 Å/min. As shown in Figure 2, there is linear relationship between the nitrogen concentration in the gate oxide film and the re-oxidizing rate. By computing the re-oxidizing rate with respect to the nitride oxide film by means of oxidizing nitriding treatment under certain conditions, the nitrogen concentration under those conditions can be determined. That is, according to the present invention, said characteristics are exploited to determine the nitrogen concentration in the oxide film without using SIMS, AES or other analysis equipment. Consequently, it is possible by means of simple and short-term film thickness measurements to evaluate the nitrogen concentration in a gate oxide film, so that operations at the manufacturing site can be managed easily, and the time and cost required for manufacturing can be reduced. Also, said re-oxidizing treatment may be performed using dry  $O_2$  as long as the atmosphere is oxidative. Also, when hydrochloric acid oxidizing treatment is performed with hydrochloric acid gas mixed in to improve the film quality, there is also an annealing effect. In addition, because said re-oxidizing causes the reaction substance to diffuse in the oxide film and causes reaction at the interface

with silicon, a thick film in which the film thickness of the re-oxidized film becomes the limiter governing rate is inappropriate. As a result, a film thickness of several hundred Å or less is preferred.

#### Effects of the invention

According to the present invention, it is possible to determine the nitrogen concentration in the gate oxide film by spot observation of the oxide film thickness without using analysis equipment, and this is an effective monitoring scheme.

#### Brief description of the figures

Figure 1 is a diagram illustrating the gate oxide film forming operation according to the present invention.

Figure 2 is a diagram illustrating the characteristics of the nitrogen and oxygen peak intensity ratio and the re-oxidizing rate determined by SIMS measurement under various oxidizing nitriding conditions.

#### Explanation of symbols

- 1 Semiconductor substrate
- 2 Thermal oxide film
- 3 Nitride oxide film
- 4 Re-oxidized film

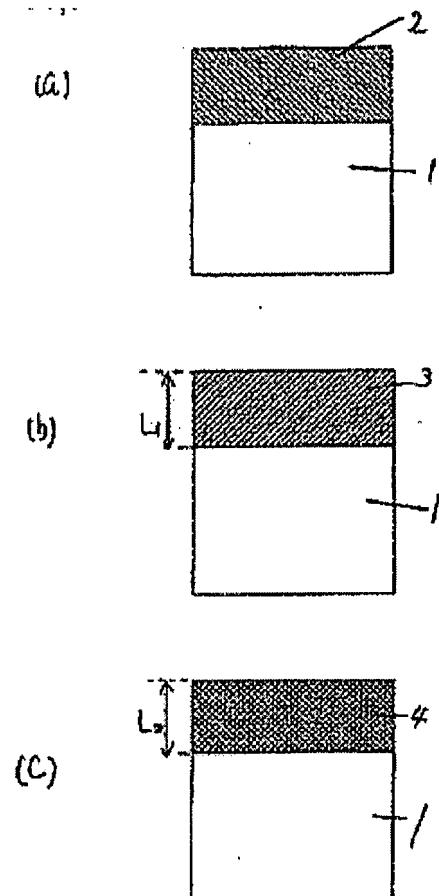


Figure 1

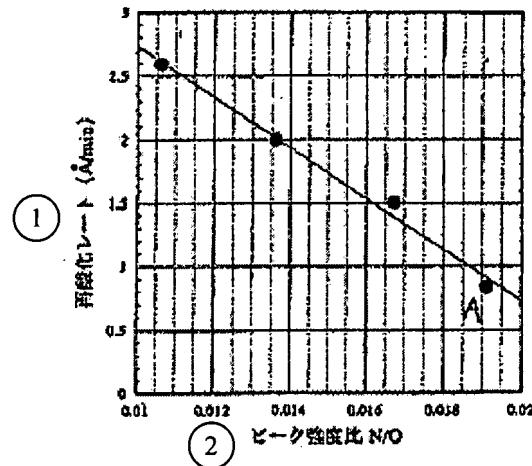


Figure 2

Key: 1 Re-oxidizing rate

2 Peak intensity ratio